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FLUORESCENT GLASSES FOR USE IN FLUORESCENTLY PUMPING ND 3(+) DO--ETC(U)
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Special Report

Contract Number N00014-81-C-2376

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FLUORESCENT GLASSES FOR USE IN FLUORESCENTLY

PUMPING Nd^{3+} DOPED LASER GLASS

AUGUST 1981

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1. INTRODUCTION

In certain cases it may be desirable to fluorescently pump a neodymium doped laser glass rather than directly excite the laser glass with the light from a flashlamp. That is, the flashlamp energy is first absorbed in a fluorescent material which then reemits to fluorescently pump the Nd^{3+} laser glass. This fluorescent pumping could be beneficial in two ways; first, the short wavelength radiation which is not efficiently absorbed by the neodymium can be converted to wavelengths which are strongly absorbed; and, second, the conversion of short wavelength pump light to longer wavelengths will minimize the amount of heat generated in the laser rod. However, if the fluorescent material is to efficiently pump the neodymium, and not simply absorb and waste the short wavelength radiation from the flashlamp, it must display several characteristics. These characteristics would be:

1. An efficient absorption at "short" wavelengths;
2. An emission at a strong Nd^{3+} absorption band;
3. A high quantum efficiency for fluorescence;
4. A short fluorescent decay time ($\tau < \tau nd$);
5. A low refractive index host.

The importance of the first three characteristics is obvious. While the fourth characteristic is only important in Q-switch applications, it will be included here since Q-switched applications are of immediate concern. (However, it is important in any application that the fluorescent decay time of the "active filter" be less than the flash lamp pump pulse). The fifth characteristic is included to minimize any trapping of fluorescence in the host. However, the importance of this is dependent on many factors which especially includes the index of refraction of any cooling liquid between the "active filter" and the laser rod.

2. FLUORESCENT GLASSES

Ions which fluoresce in glass can generally be divided into five groups. These would include:

1. The fluorescent transition metal ions;
2. The filled shell fluorescent ions;
3. The trivalent rare earths;
4. The divalent rare earths;
5. The actinides.

(Actually the trivalent rare earths, the divalent rare earths and the actinides could be considered as a single group so that there would then only be three different groups). Within these five groups there are approximately 30 ions which are known to fluoresce in glass. These ions are outlined in the attached Table 1. The most promising candidates for fluorescently pumping neodymium in glass can easily be selected from the ions listed in Table 1 by examining their known absorption and emission properties.

The Transition Metal Ions - the Mo^{3+} and Mn^{2+} ions can have reasonable quantum yields for their fluorescence. However, both ions have fluorescent decay times which are greater than one millisecond. Since this is about 3 times the decay time of the neodymium ion in a phosphate or a "high gain" silicate glass, these ions would not be suitable for fluorescently pumping a Q-switched neodymium laser. Also, the Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+} and V^{5+} ions apparently fluoresce with very low quantum yields. Therefore, none of the transition metal ions appear suitable for fluorescently pumping neodymium doped glass.

The Filled Shell Fluorescent Ions, Ce^{3+} and Eu^{2+} - These eight ions are considered together since they have a number of common characteristics. These would include: 1) all eight ions have intense allowed absorption bands in the UV region of the spectrum; 2) all except copper have allowed emissions with short decay times. (Copper has a forbidded d → s transition but still has a decay time of only 1/3 that of neodymium); 3) all have high quantum efficiencies; 4) all have broad emission bands which can be shifted significantly in different hosts. Therefore, these ions do show some promise for fluorescently pumping neodymium. However, their ability to enhance the neodymium laser efficiency would probably be limited by the fact that they primarily absorb in the UV and by their broad emission bands. These ions may in general be more useful as sensitizers.

The Trivalent Rare Earths and Uranium - Of these various ions, only the Pr^{3+}, Dy^{3+} and UO_2^{2+} ions display fluorescent decay times which are reasonable for fluorescently pumping neodymium. (Sm^{3+}, Eu^{3+} and Tb^{3+} might be considered if the system were not Q-switched. Ho^{3+}, Tm^{3+} and Yb^{3+} fluoresce at wavelengths which are too long for pumping neodymium) In addition to having reasonable decay times, the Pr^{3+}, Dy^{3+} and UO_2^{2+} ions also emit at wavelengths where the neodymium ion absorbs strongly. (For example, see the attached Figure 1 for the UO_2^{2+} emission - Nd^{3+} absorption overlap; and Figure 2 for the Dy^{3+} emission - Nd^{3+} absorption overlap.) Therefore, <u>it would appear that Pr^{3+}, Dy^{3+} and UO_2^{2+} doped glasses are the most promising candidates for fluorescently pumping neodymium doped laser glass.</u> Unknown factors are the quantum yields of the visible fluorescent bands of the Pr^{3+} and Dy^{3+} ions. (The UO_2^{2+} ion does have a high quantum yield.) Also, since the Pr^{3+} and Dy^{3+} ions do not absorb strongly at short wavelengths, sensitization by one or more of the filled shell fluorescent ions, Ce^{3+} or Eu^{2+} may be desirable.

3. OTHER POTENTIAL FLUORESCENT MATERIALS

This report is primarily a review of the various fluorescent glasses which might be used to fluorescently pump neodymium doped glass. However, glass is only one of several groups of fluorescent materials which might be used for this application. Also, since it is possible that no fluorescent glass is suitable for fluorescently pumping neodymium, a few of the limitations and promising characteristics of the other alternatives are at least briefly mentioned here.

The various broad classes of fluorescent materials would include:

1. Fluorescent organic dyes;
2. Fluorescent aromatic hydrocarbons;
3. Fluorescent chelates (both rare earth and other metals);
4. Fluorescent inorganic crystalline materials (of which there are many types);
5. Fluorescent inorganic glasses.

Organic Dyes - *Of the various materials* listed above, the organic dyes are probably the most easily tailored to meet the five important criteria given in the Introduction. However, organic dyes are notoriously unstable when exposed to the intense radiation of a flashlamp. Therefore, they would not display the long term stability desired in this application and, in general, would probably not be suitable for this application.

Aromatic Hydrocarbons - Fluorescent aromatic hydrocarbons are significantly more stable than dyes. The major limitation of these compounds would be that they generally display high energy transitions. That is, most absorb primarily in the UV with only the very large molecules extending into the blue region of the spectrum. However, these compounds may indeed be a reasonable choice for an active filter material for converting UV and blue light into longer wavelengths. In general they display strong absorption bands, high quantum yields and very short decay times (< 50 nsec).

Chelates - Fluorescent chelates generally show very strong absorption bands which are characteristic of their organic groups. However, the emission can be characteristic of either the organic group or the central metal ion. If the emission is from the metal ion (as with the rare earth chelates), the

emission characteristic are primarily defined by the metal ion. Therefore, the usefulness of the various rare earth chelates for this application can, to a large extent, be determined from the fluorescent characteristics of the rare earth in inorganic materials. However, rare earth chelates often have much lower quantum efficiencies than inorganic materials because of the back transfer of energy from the rare earth ion to the high energy C-H and O-H vibrations.

Inorganic Crystalline Materials - Fluorescent inorganic crystalline materials are extremely varied in their characteristics. A general discussion of their positive and negative characteristics is impossible in a brief paragraph. Characteristics on the positive side would include their stability to flash lamp radiation, and the very high quantum efficiency of many dopant ions. Characteristics on the negative side would include that they are often expensive to fabricate in large transparent shapes. However, some materials such as CaF_2 and Y_2O_3 are reasonably easy to fabricate into transparent polycrystalline forms; while many other fluorescent crystalline materials might be included as part of the reflective coating on the laser cavity. In general, it would appear that many more crystalline materials than glasses might be useful for this application.

REFERENCES

1. S. Parke and A. J. Watson, Phys and Chem of Glass, 10, (2), 37-42 (1969).
2. J. C. Joshi, N. C. Pandey, B. C. Joshi and Janordan Joshi, Journal of Luminescence 16, 435-440 (1978).
3. W. H. Turner and J. Eastman, J. Am. Cer. Soc. 53, 329-335 (1970).
4. P. K. Gallagher, C. R. Kurkjian and P. M. Bridenbough, Phys and Chem of Glass, 6, (3), 95-103 (1965).
5. A. D. Pearson, G. E. Peterson and W. R. Northover, J. of Appl. Physics, 37, (2), 729-734 (1966).
6. W. H. Gandy, R. J. Ginther and J. F. Weller J. Appl. Physics 38, 3030-31 (1967).
7. Yu V. Denisou, B. V. Dghurinskii and V. A. Kizel, Inorg. Materials, 3, (5), 757-61 (1967).
8. H. W. Gandy, R. J. Ginther and J. F. Weller, Appl. Phys. Letters, 6, (12), 237-39 (1965).
9. G. A. Moheeva, S. P. Lun'lein and P. P. Feofilov, J. Appl. Spectrosc. 4, (3), 175-79 (1966).
10. E. Snitzer, Phys. Rev. Letters, 7, 444-46 (1961); and others
11. L. Parke and R. S. Webb, Phys and Chem of Glasses, 13, (6), 157-160 (1972).
12. C. Hirayama and F. E. Camp, J. Electrochem Soc., 115, (12), 1275-1279 (1968).
13. S. Parke and R. S. Webb, J. Phys. D: Appl. Phys., Vol. 4, 825-828 (1971).
14. W. A. Weyl, Colored Glasses, reprinted by Dawson's of Pall-Mall, London (1959).
15. S. Parke and R. S. Webb, J. Phys. Chem. Solids, 34, 85-95 (1973).
16. A. Wachtel, J. Electrochem. Soc., 117, (5), 708-711 (1970).

Table 1. Ions With Fluoresce in Glass

Transition Metal Ions

	Reference
Mo^{3+}	1
Mn^{2+}	3
Cr^{3+}	
Fe^{2+}	12
Co^{2+}	12
Ni^{2+}	12
V^{5+}	14

Filled Shell Fluorescent Ions

	Reference
Cu^{+}	11
Ag^{+}	14
Sn^{2+}	13
Pb^{2+}	15
Sb^{3+}	13
Bi^{3+}	15
$T\ell^{+}$	15

Trivalent Rare Earths

Ce^{3+}	Tb^{3+}
Pr^{3+}	Dy^{3+}
Nd^{3+}	Ho^{3+}
Sm^{3+}	Er^{3+}
Eu^{3+}	Tm^{3+}
Gd^{3+}	Yb^{3+}

Divalent Rare Earths

	Reference
Eu^{2+}	16
Yb^{2+}	16
Sm^{2+}	16

Actinide

UO_2^{2+}

Table 2. Fluorescent Decay Times of Filled Shell, Rare Earth, and Actinide Ions in Glass

		τ (Millisec)	Reference			τ (Millisec)	Reference
*	Ce^{3+}	0.0001		*	Tl^{+}	0.003	15
*	Pr^{3+}	0.2	9	*	Pb^{2+}	0.003	15
	Nd^{3+}	0.3-0.8	10	*	Sn^{2+}	0.008	13
	Sm^{3+}	1.0	7	*	Sb^{3+}	0.005	13
	Eu^{3+}	2.5	4	*	Bi^{3+}	0.003	15
	Gd^{3+}	4.2	5	*	Cu^{+}	0.10	11
	Tb^{3+}	2.5	5,7		---------		
*	Dy^{3+}	0.5	7				
	Ho^{3+}	1.0 (at 2μ)	8	*	UO_2^{2+}	0.20	2,14
	Er^{3+}	10.0 (at 1.5μ)	6				
	Tm^{3+}	0.5 (at 1.8μ)	6				
	Yb^{3+}	1.0	6,8				
	---------						
*	Eu^{2+}	0.002					
	Yb^{2+}	?					
	Sm^{2+}	?					

Table 3. Possible Low Index Glasses for Use in Fluorescent Pumping Applications

SiO_2	74.91	61.94	46.30
B_2O_3	12.45	25.82	42.33
Na_2O	11.26	11.19	10.44
CaO	0.10	0.14	0.08
Al_2O_3	0.89	0.84	0.80
N_d	1.495	1.489	1.485

1,2 - Ethonediol)
Ethylene glycol) $N_d = 1.4314^{20}$
Glycol)

Water $N_d = 1.333$

Figure 1. UO_2^{2+} Doped Glass Absorption and Emission Spectra (Showing the UO_2^{2+} Emission – Nd^{3+} Absorption Overlap).

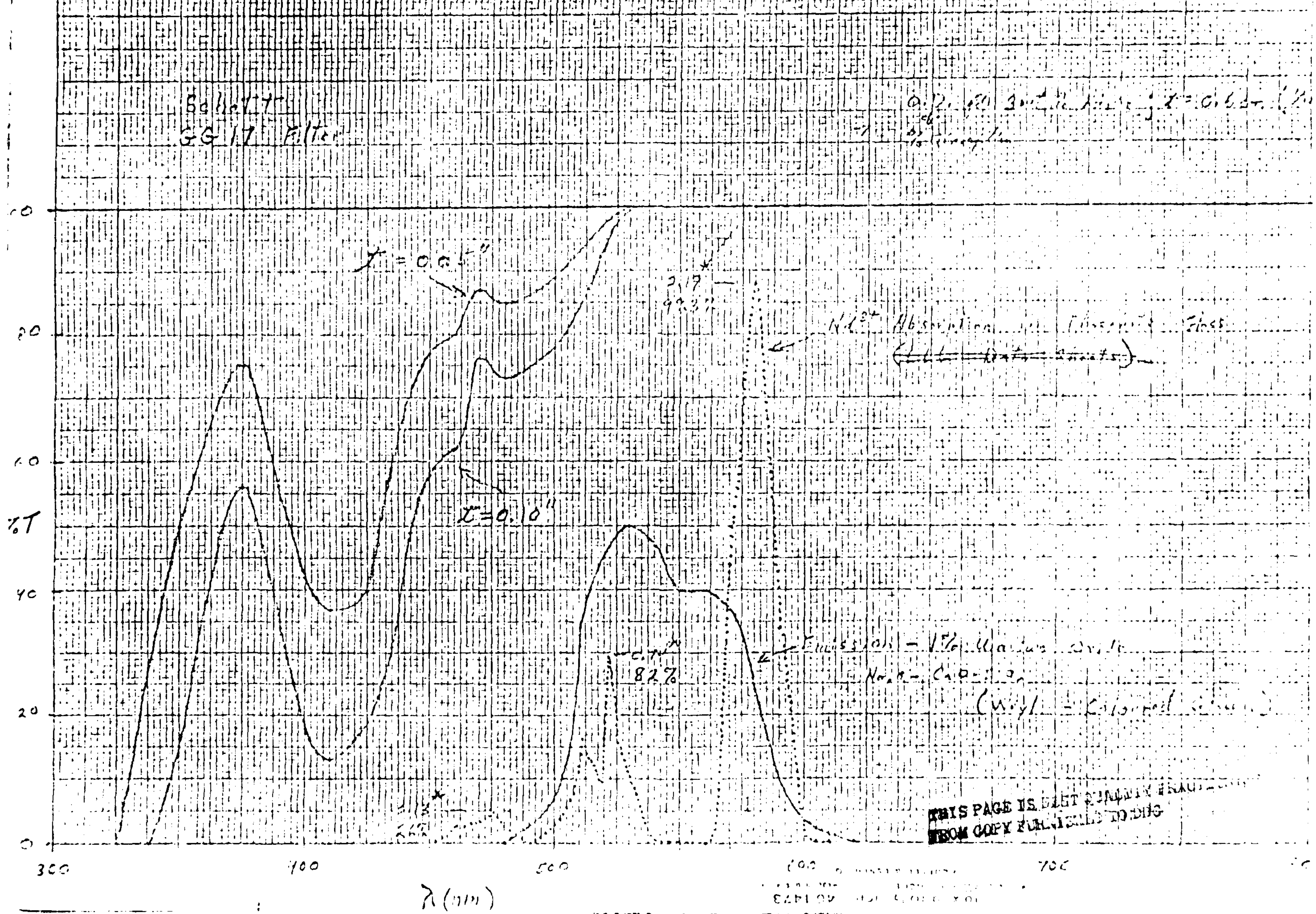

Figure 2. Dy^{3+} Doped Glass Absorption and Emission Spectra (Showing the Dy^{3+} Emission – Nd^{3+} Absorption Overlap).